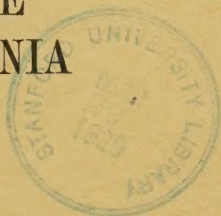


THE AMMINES OF MAGNESIUM
PERCHLORATE

AND

A NEW METHOD FOR THE
DETERMINATION OF AMMONIA



DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE RE-
QUIREMENTS FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY IN THE FACULTY OF
PURE SCIENCE, COLUMBIA
UNIVERSITY.

By
WILLARD R. LINE



NEW YORK CITY
1928

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UNCLASSIFIED
Dissertation

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ACKNOWLEDGMENT

The author desires to express his gratitude to Professor H. T. Beans for his helpful criticism of the general plan of this investigation and for assistance given in the completion of the work.

THE AMMINES OF MAGNESIUM PERCHLORATE

An investigation upon the preparation and properties of anhydrous magnesium perchlorate by Willard¹ showed that this substance combines vigorously with water forming a trihydrate and a hexahydrate. The anhydrous salt was shown to be as effective as P_2O_5 in the removal of water from moist air with a rate of flow up to 5 liters per hour. The trihydrate was equally efficient at $0^\circ C$ but not quite so at higher temperatures.

In a vast number of hydrates the water is replaceable by ammonia and it seemed likely in this case also that anhydrous $Mg(ClO_4)_2$ would add ammonia and probably form a hexammine as well as other intermediate ammines.

Preliminary experiments showed that anhydrous magnesium perchlorate does combine vigorously with ammonia with the evolution of much heat and a large increase in volume and the present investigation was undertaken to determine the composition of the compounds formed and their relative stabilities.

This investigation includes the preparation of $Mg(ClO_4)_2 \cdot 6NH_3$ and $Mg(ClO_4)_2 \cdot 2NH_3$, the determination of their composition and the measurement of their densities from which the molecular volumes are calculated. Thermal studies include the determination of the vapor pressure curve for the equilibrium between the two compounds and the isothermal decomposition of the hexammine into the diammine. A study of the behavior of the two ammines when treated with acid has resulted in the development of a new method for the determination of ammonia.

In recent years Biltz,² Ephraim,^{3, 4, 5} Clark^{6, 7} and others have reported results of investigations which have dealt to a considerable extent with the attempts to discover and define the various factors influencing the stability of co-ordination compounds of this type. Among the factors considered

are the dimensional relationships of the cation, anion and neutral molecule (water, ammonia, etc.) present in these compounds. The relative stabilities are indicated experimentally by determining the temperatures at which the vapor pressures of the various ammines all reach a certain value, usually 100 or 760 mm is used.

Table I shows the temperatures in degrees Centigrade at which the vapor pressures reach 100 mm for the chloride hexammines of some closely related bivalent metals, Clark.⁷

TABLE I.

Metal	Ni	Co	Fe	Cu	Mn
At. vol.	6.59	6.77	7.12	7.12	7.43
Hexamine stability					
$t_p=100$ mm	125°	90°	71°	66°	45°

These temperatures are taken as indicating experimentally that the order of decreasing stability of these hexammines is Ni—Co—Fe—Cu—Mn.

In general, the influence of the dimensions mentioned above upon stability is as follows: stability decreases with increase in the atomic volume of the cation and molecular volume of the neutral molecule and with decrease in the atomic or molecular volume of the anion. The influence of the atomic volume of the cation is seen in Table I where atomic volumes increase from Ni to Mn and the stabilities fall off in the same order.

The general effect of the anion is seen in Table II where the stabilities of the hexamine halides of nickel and of cobalt are compared. With increasing atomic volume of the halogen the stability of the hexamine increases, Clark.⁷

TABLE II.

Compound	$t_p=100$ mm	Compound	$t_p=100$ mm
Ni(NH ₃) ₆ Cl ₂	125°	Co(NH ₃) ₆ Cl ₂	90°
Ni(NH ₃) ₆ Br ₂	160°	Co(NH ₃) ₆ Br ₂	121°
Ni(NH ₃) ₆ I ₂	177°	Co(NH ₃) ₆ I ₂	141°

In Table III are compared the stabilities of compounds having the same cation and anion but a varying neutral molecule. As indicated above, the stabilities decrease with increasing size of the neutral molecule, Clark.⁷

TABLE III.

Molecular group	No. mols. with NiI_2	Mol. vol. of mol. group	Stability $t_p=100$ mm
NH_3	6	28.47	236°
$\text{NH}_2(\text{CH}_3)$	6	44.34	203.5°
$\text{NH}_2(\text{C}_2\text{H}_5)$	6	63.73	102.5°
$\text{NH}(\text{CH}_3)_2$	6	65.59	25°

This generalization is not without exceptions, in fact, there are numerous exceptions, but in the case of the hexammines and particularly in series of compounds with closely related cations and anions it holds well and is a useful guide in the study of these compounds. In connection with the present investigation, for example, it seemed likely that $\text{Mg}(\text{ClO}_4)_2$ would form a stable hexammine. Ephraim³ states that an element of atomic volume greater than 14 will not form stable hexammines and Clark⁷ that the co-ordination number 6 is usually associated with bivalent ions of metals with atomic volumes less than 14. In the case of magnesium (atomic volume 14) it is a question, Biltz,⁸ whether its halides form true hexammines or mixed crystals approximating them in composition in which the ammonia is loosely bound like the water in zeolites. In $\text{Mg}(\text{ClO}_4)_2$ we have a cation whose atomic volume is 14 combined with an anion of relatively large molecular volume and it seemed probable that the large volume of the perchlorate ion might more than compensate for the large atomic volume of magnesium and that a stable hexammine would be formed. This is shown to be the case and $\text{Mg}(\text{ClO}_4)_2$ does form the stable $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$ as well as the still more stable $\text{Mg}(\text{ClO}_4)_2 \cdot 2\text{NH}_3$.

PREPARATION OF MATERIALS.

Perchloric Acid. Perchloric acid was prepared by Willard's⁹ method by the oxidation of ammonium perchlorate with a mixture of nitric and hydrochloric acids after which the solution was evaporated to fumes and distilled in vacuo. The use of a distillation apparatus with ground glass connections, as recommended by Willard, is to be emphasized. A cork connection between the air and water condensers was used for

some time until during one distillation a small amount of hot acid came in contact with the cork resulting in a loud detonation which forced the cork some distance up the air condenser. No further damage was done but an all-glass system was used thereafter.

Magnesium Perchlorate, Hexahydrate. This salt was prepared in two ways: By treating magnesium oxide with a slight excess of perchloric acid, Willard¹ and by boiling a solution of ammonium perchlorate containing an excess of magnesium oxide in suspension for three to four hours, replacing the water as it evaporated, until no test was given for ammonia with Nessler's reagent and then adding perchloric acid to dissolve the remaining oxide. The first method is to be preferred because of the purer product obtained and was the one used for the preparation of the magnesium perchlorate used in this investigation. The second method is convenient if a product of high degree of purity is not needed and a large quantity of perchloric acid is not available. Because of the large solubility of magnesium perchlorate in water, however, (73.453 gm. per 100 cc of solution at 25°C), Willard,¹ recrystallization does not remove the impurities present in the raw materials. One slight modification was made in Willard's method since it was found that some of the magnesium oxide used contained small amounts of iron and aluminum. A suspension of magnesium oxide in water was treated with a little less than the calculated amount of dilute perchloric acid. After boiling a few minutes the solution was filtered leaving the aluminum and iron in the paper with the excess oxide. The slightly alkaline solution was acidified with perchloric acid and evaporated until fumes of perchloric acid were given off and then allowed to cool with the addition of sufficient water to keep the mass semifluid. After filtering with suction and washing with small portions of ice-cold water the salt was recrystallized two or three times.

Magnesium Perchlorate, Anhydrous. At first anhydrous magnesium perchlorate was prepared according to Willard¹ by heating the hexahydrate to about 170°C in a current of dried air until most of the water had been removed and then

raising the temperature to 250°C. Dried in this way the material melts and becomes heavily encrusted necessitating frequent stirring and grinding and the dehydration is very slow. Later it was found that small samples could be prepared in much shorter time by applying a high vacuum to the hexahydrate at room temperature and slowly raising the temperature to 250°C. Prepared in this way all liquefaction is avoided, no stirring or grinding is necessary and the product is finely granular and neither cakes nor adheres to the flask.

Magnesium Perchlorate, Hexammine. The hexammine was prepared by two methods. Dried ammonia gas was passed over anhydrous magnesium perchlorate at room temperature. A vigorous reaction takes place, considerable heat is evolved accompanied by a large increase in volume. At the end of one to three hours the reaction is complete and a fine, white voluminous powder is obtained which contains 6 moles of ammonia. Most of the hexammine used in this investigation was prepared in this way. In the second method, the hexahydrate was partially dehydrated and then alternately treated with dried ammonia at room temperature and heated to 250° with a vacuum. The water of the hexahydrate can be completely replaced by ammonia by this process.

Magnesium Perchlorate, Diammine. The diammine was prepared from the hexammine by isothermal decomposition. Weighed samples of the hexammine were prepared in the closed system.* The system was evacuated and the flask heated in an oil bath to an automatically controlled temperature. When the equilibrium pressure had been established, usually within a half-hour, the flask was removed, cooled and weighed. The ammonia was then removed from the system with a pump and the heating repeated until equilibrium was again established. This procedure was repeated until upon heating at the given temperature equilibrium was established at a lower pressure. The loss in weight showed that the hexammine when decomposed isothermally in this way yields the diammine without any intermediate steps.

* See p. 16.

PROPERTIES.

Magnesium Perchlorate, Hexahydrate. The properties of this salt have been described by Willard.¹ A water solution of the salt is not neutral as he states but gives a transition color with methyl red. This is what would be expected considering the base and acid from which it is derived. The density of the hexahydrate determined by the displacement of toluene is 1.976 at 20°/4° which agrees well with Willard's value of 1.970 at 25°/4° using carbon tetrachloride.

Magnesium Perchlorate, Hexammine. The hexammine as prepared above is a light, fine white powder. When the excess ammonia is removed from the preparation flask by passing dry air through it or by applying a vacuum at low temperature, the hexammine has only a slight odor of ammonia. At room temperature the hexammine has an ammonia pressure of only 1–2 mm. Exposed to air, however, the odor becomes more pronounced in a short time due to the gradual displacement of ammonia by moisture in the atmosphere. One sample of the hexammine after standing nearly a year had no odor of ammonia but was shown to contain two moles by titration.

In an atmosphere of ammonia (approximately 760 mm) the hexammine is stable nearly up to its melting point which is at 235°C. At this temperature it dissociates into the diammine and ammonia. As the ammonia escapes from the melt or is drawn off with a pump the material solidifies again. When melted and allowed to cool it sets to a hard, white, glassy cake. Dry ammonia acts very quickly upon the surface forming a fine white powder and soon the entire mass is reconverted quantitatively to the hexammine with a large increase in volume.

The ammonia in the hexammine and in the diammine can be determined quantitatively by adding an excess of standard acid and back titrating with standard base using methyl red as the indicator.

When put into water hydrolysis occurs and magnesium hydroxide is precipitated. The density determined by the displacement of toluene is 1.41 at 20°/4°.

Magnesium Perchlorate, Diammine. The diammine prepared from the hexammine is a fine, white powder much less voluminous than the hexammine. It has no odor of ammonia and even at 200°C has an ammonia pressure of only 3 mm. At 250°C the ammonia pressure is 7 mm. When heated above this temperature decomposition of the perchlorate radical occurs. This seems to indicate that the diammine upon dissociation goes directly to the anhydrous salt without the intermediate formation of a monammine. Willard has found and it has been the writer's experience that if the anhydrous salt is heated above 250°C decomposition sets in. Both the hexammine and the diammine have been heated for short intervals up to 300°C without any decomposition of the perchlorate radical taking place. If that temperature, however, is held long enough, for example as in trying to establish equilibrium, decomposition occurs. Since the presence of ammonia apparently stabilizes the salt towards heat it seems reasonable to expect that if a monammine were formed it would be somewhat more stable than the anhydrous salt. From the fact that the diammine heated to a temperature at which the anhydrous salt begins to decompose also suffers decomposition of the perchlorate radical, it is concluded that a monammine is not formed.

When put into water hydrolysis occurs and magnesium hydroxide is precipitated as in the case of the hexammine. The density from displacement of toluene is 2.053 at 20°/4°.

ANALYTICAL DATA.

Table IV gives representative analytical data obtained in the preparation and analysis of $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$ and $\text{Mg}(\text{ClO}_4)_2 \cdot 2\text{NH}_3$ together with the same values calculated from the formulas.

DETERMINATIONS MADE AND METHODS EMPLOYED.

Water in $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was determined by loss in weight when samples of the salt were heated in vacuum to constant weight.

Magnesium in $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$ were determined by precipitating and weighing as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$.

Ammonia in $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$ was determined

(a) by the increase in weight when ammonia was added to the anhydrous salt.

(b) by titration with HCl and NaOH using methyl red as the indicator.

Ammonia in $\text{Mg}(\text{ClO}_4)_2 \cdot 2\text{NH}_3$ was determined

(a) by loss in weight when the hexammine was decomposed isothermally.

(b) by titration with HCl and NaOH using methyl red.

TABLE IV.

Determination. Water in $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$.

Method. Loss in weight when dried at 250°C in vacuum.

Found	Calculated
%	%
32.67	32.63
32.59	
32.63	
32.62	
32.61	
32.67	
32.62	
32.65	
Mean = 32.63	
av. dev. = .7 pts./1000	

Determination. Magnesium in $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$.

Method. Weighed as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$.

Found	Calculated
%	%
7.32	7.34
7.38	
Mean = 7.35	

Determination. Magnesium in $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$.

Method. As above.

Found	Calculated
7.60	7.47
7.62	
7.48	
Mean = 7.55	

TABLE IV. (*continued*).

Determination. Ammonia in $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$.
 Method. Increase in weight when ammonia was added to the anhydrous salt.

Found	Calculated
%	%
31.34	31.40
31.45	
31.41	
31.33	
31.32	
31.42	
31.36	
31.32	
31.48	
31.39	
31.48	
31.45	
31.49	
31.39	
Mean = 31.40	
av. dev. = 1.4 pts./1000	

Determination. Ammonia in $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$.

Method.	Titration.
31.28	31.40
31.12	
31.15	
31.29	
31.29	
31.31	
31.16	
31.29	
31.28	
31.31	
31.37	
Mean = 31.26	
av. dev. = 2.0 pts./1000	

Determination. Ammonia in $\text{Mg}(\text{ClO}_4)_2 \cdot 2\text{NH}_3$.

Method.	Loss in weight during isothermal decomposition.
Found	Calculated
%	%
13.40	13.24
13.38	
13.42	
Mean = 13.40	

TABLE IV. (*continued*).

Determination.	Ammonia in $\text{Mg}(\text{ClO}_4)_2 \cdot 2\text{NH}_3$.	
Method.	Titration.	
	13.19	13.24
	13.33	
	13.25	
Mean	= 13.26	

DENSITY DETERMINATIONS.

The densities of $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{ClO}_4)_2$, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$, and $\text{Mg}(\text{ClO}_4)_2 \cdot 2\text{NH}_3$ were determined at 20°C by the picnometer method using toluene.

MATERIALS AND APPARATUS.

The toluene had been washed with concentrated H_2SO_4 and NaOH solution, dried with CaCl_2 and sodium wire and then distilled. At the time the densities were determined it had stood several months in contact with sodium wire. It was redistilled before use and the middle fraction boiling at 110 – 111°C was collected. Its density at $20^\circ/20^\circ$ was .8655.

The picnometer, made of pyrex, had a capacity of about 11 cc. It was flask-shaped with a ground glass capillary stopper and cap. A similar picnometer was used throughout as a tare. During a period of several days before they were put into use both picnometers, together with stoppers and caps, were alternately steamed for thirty minutes and dried for an hour or more at 150°C . After each density determination both picnometers were steamed and dried in this way. The mean value of 18 consecutive weighings (against the tare) of the picnometer used was 0.3092 gm. with an average deviation of 0.4 pts./1000. The picnometer was calibrated with freshly boiled redistilled water.

A water bath containing a cooling coil and electrically heated and stirred was employed to bring the picnometer to constant temperature. The temperature of the bath was maintained at 20°C by means of a bi-metallic regulator and never varied more than 0.02° and over long periods the variation was less. The temperature of the room and balance case was kept 1 – 2 degrees below 20° to avoid expansion of the toluene after the picnometer had been removed from the bath.

GENERAL PROCEDURE.

The general procedure was to weigh some of the finely powdered material in the picnometer and then to fill it about three quarters full of toluene. The picnometer with sample and toluene was placed in a small vacuum desiccator and a vacuum applied for about 20 minutes to remove occluded air after which it was filled with toluene, the stopper and cap inserted and placed in the water bath for 30 minutes. At the end of this time the excess liquid was absorbed with filter paper, the picnometer removed from the bath, wiped off (as was also the tare) and allowed to stand in the balance case about 20 minutes before weighing. After each weighing the stopper was removed, the picnometer again filled to the top with toluene and the above operations repeated. From 5-8 weighings were made on each sample in this way.

Samples of toluene taken from the picnometer at the end of a determination gave no residue when evaporated showing that the salts were insoluble in it. All weighings were reduced to vacuo.

The thermometers used here and in other portions of this work were checked against the laboratory standards which had been calibrated at the Bureau of Standards.

The results obtained are shown in Table V.

TABLE V.

Compound	Density 20°/4°	Mean
$\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.976	1.976
	1.975	
$\text{Mg}(\text{ClO}_4)_2$	2.529	2.53
	2.540	
	2.516	
$\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$	1.402	1.41
	1.416	
$\text{Mg}(\text{ClO}_4)_2 \cdot 2\text{NH}_3$	2.051	2.053
	2.054	

DISCUSSION.

The density of the hexahydrate was determined on samples taken from two different lots of the salt. The values obtained compare well with Willard's ¹ value of 1.970 at 25°/4° in carbon tetrachloride.

The density for $\text{Mg}(\text{ClO}_4)_2$ is lower than Willard's value of 2.60 at 25°/4° in carbon tetrachloride. The anhydrous salt is very hygroscopic and the difference may be due to taking on moisture during the filling and weighing of the picnometer in spite of the following precautions which were taken. The anhydrous salt was heated to above 200°C and put into the picnometer while the latter was inside an oven also above 200°. The stopper was inserted and the picnometer allowed to cool in a desiccator containing anhydrous $\text{Mg}(\text{ClO}_4)_2$.

As has been noted previously the hexammine in contact with moist air gives up ammonia readily and the lack of concordance in the results for this salt may be due to this fact.

The molecular volumes of the anhydrous salt, the hexahydrate and the two ammines and the apparent volume of the water and ammonia in the complexes have been calculated from the density determinations. These results are shown in Table VI. The apparent volume of the water (or ammonia) is calculated by subtracting the molecular volume of the anhydrous salt from that of the hydrate (or ammine) and dividing the result by the number of molecules of water (or ammonia) in the complex.

The apparent volumes so obtained agree well with the values found for other salts. For the hexammines of bivalent cobalt salts, for example, Biltz ¹⁰ gives the ammonia volume in the chloride as 20, in the bromide as 21 and in the iodide as 24. The water volume in both the cobalto and cobalti series given by Biltz ¹⁰ and Clark ⁶ is about 14 varying between 13.7 and 15.2.

It would be of interest to compare these volume relationships with those of the corresponding compounds of the magnesium halides. Unfortunately the only density data available is on MgCl_2 and its hexahydrate and is shown in Table VI. The densities of the ammines have not been determined.

TABLE VI.

Compound	Molecular weight	Density	Molecular volume	Apparent volume of H ₂ O or NH ₃
Mg(ClO ₄) ₂	223.2	2.60	85.8	
Mg(ClO ₄) ₂ .6H ₂ O	331.3	1.976	167.7	13.7
Mg(ClO ₄) ₂ .6NH ₃	325.4	1.41	230.8	24.2
Mg(ClO ₄) ₂ .2NH ₃	257.3	2.053	125.3	19.8
MgCl ₂	95.23	2.320	40.75	
MgCl ₂ .6H ₂ O	203.33	1.569	129.2	14.7

TEMPERATURE-PRESSURE-COMPOSITION EQUILIBRIA.

Experimental studies upon ammines by Biltz,² Ephraim,³ Clark⁷ and others have usually included temperature-pressure-composition equilibria from which the formation of definite compounds has been confirmed and their relative stabilities determined. In the present work the vapor pressure curve and the isotherm for the equilibrium between Mg(ClO₄)₂.6NH₃ and Mg(ClO₄)₂.2NH₃ have been experimentally determined. It was not possible to make a similar determination for the equilibrium between Mg(ClO₄)₂.2NH₃ and Mg(ClO₄)₂ because of the decomposition of the anhydrous salt at temperatures at which the diammine showed an appreciable ammonia pressure. Isobars could not be determined because the melting point and decomposition temperature (both about 235°C) of the hexammine under an ammonia pressure of one atmosphere were so nearly coincident that it was impossible to establish equilibrium. When a sample of the hexammine was heated in an atmosphere of ammonia at atmospheric pressure no loss in weight occurred until a temperature of 235°C was reached. At this temperature both melting and decomposition took place. The loss in weight in successive determinations was not constant even with prolonged heating. The isotherm shows a sharp transition from the hexammine to the diammine. The melt obtained here probably consisted of a solution of these two salts together with free ammonia.

APPARATUS.

The apparatus employed was essentially that described by Clark⁷ modified in but one minor detail, namely: an opening with a ground glass stopper was placed in the KOH-trap to facilitate filling and cleaning. The entire apparatus was made of pyrex. It consisted of a preparation flask having a total volume of about 50 cc connected by a wide side-arm having a ground glass joint to a trap containing fused KOH and thence to a tube bearing three stopcocks and connected to a manometer. The side-arm of the preparation flask was made wide enough to permit the introduction of the sample. The top of the flask was closed with a stopcock to which was joined a narrow tube running nearly to the bottom of the flask and through which ammonia was introduced into the system. Several preparation flasks were made and the side-arms of all were ground to fit the neck of the trap. Each flask had a stopper ground to fit the side-arm. The major purpose of the design was to secure a piece of apparatus in which the anhydrous salts and ammines might be prepared and studied without the necessity of transfer of the sample or exposure to moisture. Since many of these substances are extremely hygroscopic this is of prime importance.

The oil bath of about 5 liters capacity was electrically heated and stirred. Temperature was controlled to within 0.1° by a mercury thermoregulator. The bath was filled with heavy lubricating oil known as "Heavy Navy Mineral." It proved very satisfactory producing very little smoke even up to 230°C . For stirring, a Dictaphone motor with rheostat attached was used. Six of these motors have been in use almost constantly for about four years and have been found very useful for light work. They can be adjusted through a wide range of speed, are free from noise and have given no trouble whatever.

Anhydrous $\text{Mg}(\text{ClO}_4)_2$ was sometimes prepared in the apparatus described but usually a preparation flask with the hexahydrate was heated in an auxiliary, electrically heated air bath while an ammine was being prepared or studied in the main apparatus.

TEMPERATURE-PRESSURE EQUILIBRIUM. VAPOR PRESSURE.

Samples of $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were converted to the anhydrous salt by heating up to 250°C in a vacuum until the weight was constant. Then, after connecting to the KOH-trap, a slow stream of ammonia gas, delivered from a cylinder and dried by passage through towers filled with soda-lime and potassium hydroxide, was passed over the sample at room temperature to constant weight. The apparatus was evacuated at room temperature and the manometer and barometer read. The temperature was raised and held at about 15–20 degree intervals until equilibrium was established. Equilibrium was usually attained within 5 to 10 minutes after the temperature had been changed but it was always held 20 minutes longer before the final reading was taken. Individual points were checked from both the low and high sides and at the end of the day or run the heat was turned off and the system left closed. Invariably the manometer returned to its initial position within 12 hours unless a leak developed in the system.

A typical set of data is given in Table VII and also a curve, Curve 1, prepared from 4 different runs.

TABLE VII.
Temperature-Pressure Equilibrium between
 $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$ — $\text{Mg}(\text{ClO}_4)_2 \cdot 2\text{NH}_3$.
These points are shown on Curve 1 by unshaded circles.

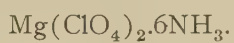
Temperature °C	Pressure mm.
21.1	1
51.8	1
70.2	2
85.0	3
105.1	7
125.3	16
148.5	48
168.7	108
180.1	161
189.7	224
199.4	304
206.1	367
206.8	374
209.6	413
225.0	699

In Table VIII the stability of $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$ is compared with the same values given by Biltz² for the highest ammines of the halides of magnesium. The analytical figures showed these ammines to be $\text{MgCl}_2 \cdot 6\text{NH}_3$, $\text{MgBr}_2 \cdot 6\text{NH}_3$ and $\text{MgI}_2 \cdot 6\text{NH}_3$ but from their abnormal behavior when heated Biltz concluded that he was dealing with mixed crystals. He was unable to determine the vapor pressure curves directly and sketched them in from points obtained by the isothermal decomposition. Using this data the stability of $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$ lies between that of the bromide and the iodide. The molecular volume of the ClO_4 ion calculated from that of the anhydrous salt by subtracting the atomic volume of magnesium is about 36 while that of the iodide ion is 25.7, Biltz.² Considering the volumes of the anions, the perchlorate ammine would be expected to have a higher stability than the iodide ammine. Before drawing any conclusion, however, better data on compounds more closely related to $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$ is desired as, for example, on the ammines of magnesium chlorate.

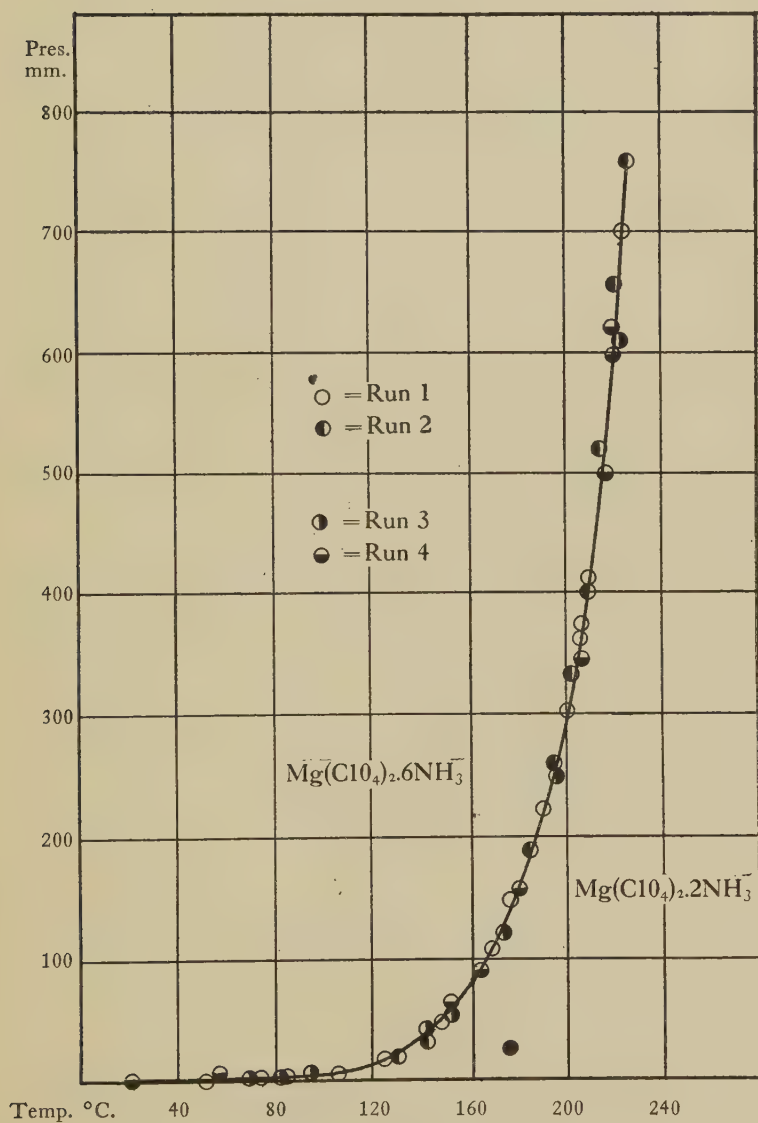
TABLE VIII.

Compound	$t_p=100$ mm
$\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$	168°
$\text{MgCl}_2 \cdot 6\text{NH}_3$	94°
$\text{MgBr}_2 \cdot 6\text{NH}_3$	147°
$\text{MgI}_2 \cdot 6\text{NH}_3$	202°

TEMPERATURE-PRESSURE EQUILIBRIUM.



Curve 1.



TEMPERATURE-COMPOSITION EQUILIBRIUM. ISOTHERM.

A flask containing a weighed amount of the hexammine was placed in the oil bath, connected with the manometer system and evacuated. The bath was then heated to 148.1°C . When equilibrium had been established and maintained for at least 15–30 minutes, the manometer and barometer were read from which the ammonia pressure was determined. The flask was then either removed from the bath and, after cooling to room temperature, weighed or the system was again evacuated and equilibrium again established before weighing. After weighing, the flask was returned to the system and the evacuation, heating and weighing repeated until equilibrium was established at a lower pressure. At the end of the run the sample was reammoniated and a second determination at the same temperature was made. Two additional determinations were made at a higher temperature, 168.3 – 168.5°C .

These determinations show that $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$ yields a diammine without the formation of any other intermediate compounds. Reasons have been stated earlier in this report for the belief in the non-existence of a monammine. If that conclusion is valid $\text{Mg}(\text{ClO}_4)_2$ resembles MgI_2 more than MgBr_2 or MgCl_2 . The isothermal decomposition of the hexammine magnesium halides showed, Biltz and Hüttig,⁸ that the chloride and bromide yield a diammine and monammine and the iodide a diammine only.

The results are shown in Table IX and Curves 2 and 3.

TABLE IX.
Isothermal Decomposition of $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$.

Sample K 1. Run 1.

Temp. °C	Pres. mm.	Wt. Sample gms.	NH_3 gm.	NH_3 mols.
148.1	49	1.886	.589	5.95
148.1	50	1.811	.514	5.20
148.0	50	1.652	.355	3.59
148.0	11	1.505	.208	2.10
148.1	5	1.498	.201	2.03

Sample K 1. Run 2.

148.3	50	1.886	.589	5.95
148.2	49	1.779	.482	4.87
148.3	49	1.695	.398	4.02
148.2	49	1.680	.383	3.87
148.2	49	1.625	.328	3.32
148.3	48	1.574	.277	2.80
148.2	48	1.564	.267	2.70
148.3	48	1.525	.228	2.30
148.3	21	1.506	.209	2.11
148.1	1	1.501	.204	2.06
148.1	4	1.501	.204	2.06

Sample K 1. Run 3.

168.3	106	1.886	.589	5.95
168.3	104	1.710	.413	4.17
168.4	104	1.544	.247	2.50
168.3	107*	1.527	.232	2.35
168.3	3	1.498	.201	2.03

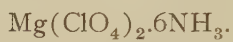
Sample K 1. Run 4.

168.4	104	1.886	.589	5.95
168.5	104	1.646	.349	3.53
168.5	104	1.579	.282	2.85
168.5	103	1.564	.267	2.70
168.5	33	1.514	.217	2.19
168.5	3	1.498	.201	2.03

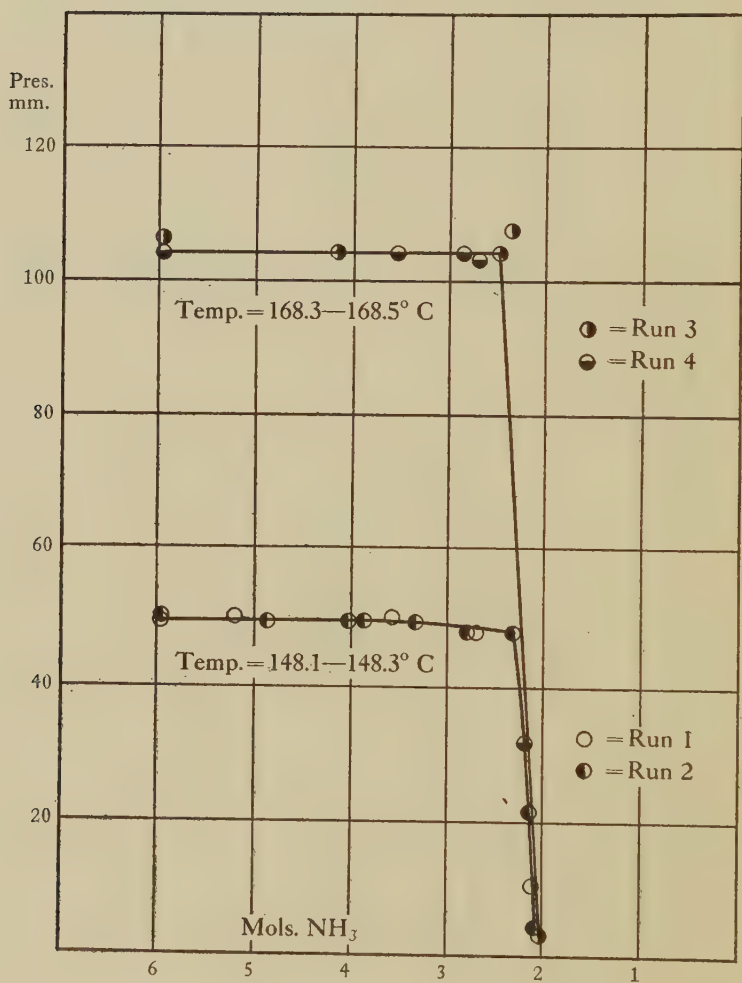
* While adjusting the thermoregulator the temperature of the bath went to 175°C for a short time. Equilibrium probably not established when this reading was made.

ISOTHERMAL DECOMPOSITION

OF



Curves 2 and 3.



A NEW METHOD FOR THE DETERMINATION OF AMMONIA

In view of the behavior of magnesium perchlorate and its hydrates toward ammonia and from the results obtained in the titration of the ammonia in its amines, it was considered probable that this material could be used for the quantitative determination of ammonia.

Two procedures were used. One procedure was to absorb the ammonia evolved from an ammonium salt in a weighed amount of magnesium perchlorate, the increase in weight giving directly the amount of ammonia. A second procedure was to absorb the evolved ammonia in magnesium perchlorate and determine the quantity by titration with standard acid. Both methods gave satisfactory results. Each method possesses certain advantages over the other to which reference will be made later.

THE ABSORBENT.

The choice between anhydrous magnesium perchlorate and its trihydrate was made in favor of the latter largely because this material is already on the market under the trade name "Dehydrite" and has been recommended for the absorption of water in organic combustions, Smith.¹¹ The physical character of Dehydrite resembling soda-lime, makes it better suited as an absorbent than the pulverulent anhydrous salt. Preliminary experiments showed that the trihydrate would absorb ammonia. When dry ammonia gas was passed over or through the trihydrate to saturation, water was observed to condense in the tube beyond the absorbent indicating that some of the water, at least, had been replaced by ammonia. This also showed that if the procedure of weighing the ammonia was to be used a large excess of the trihydrate would be required to insure the retention of the water so replaced. Two lots of Dehydrite were used and both were found to be slightly alkaline so that when the titration method was used a blank correction had to be made for the acid used up by the absorbent. Each lot seemed to be uniform throughout but they differed

somewhat in alkalinity. Lot A required 0.15 cc of 0.1 N HCl per gram and Lot B 0.24 cc of the same acid per gram of Dehydrite. In general, 3-4 grams of Dehydrite were used in each tube if the contents were to be titrated. This was a very liberal excess and probably could be diminished considerably if a U-tube of smaller diameter were used so as to obtain a longer column of absorbent.

In addition to the commercial Dehydrite an absorbent approximating the trihydrate in water content, prepared from recrystallized magnesium perchlorate hexahydrate, was used as a check upon both procedures. The same results were obtained as with the Dehydrite. No blank was needed with this material.

SOURCES OF AMMONIA.

Two substances were used as the source of ammonia: NH_4Cl and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. The ammonium chloride of a C. P. grade was sublimed and then crystallized three times from water. Its ammonia content, as determined by distillation with NaOH and subsequent titration checked the theoretical value satisfactorily.

Ammonium magnesium phosphate of C. P. grade was dissolved in dilute HCl, filtered and reprecipitated following the conditions given by Fales¹² and, after filtering with suction was washed with alcohol and ether and the ether allowed to evaporate at room temperature. The ammonia content, determined by distillation and titration, was lower than the theoretical. This material was selected as being a source of both ammonia and water since it was thought that on occasion it might be desired to determine both constituents on the same sample. In such a case both water and ammonia could be absorbed in Dehydrite, the increase in weight determined, the ammonia titrated and the water determined by difference. Or, the water and ammonia could be absorbed in separate tubes, one containing KOH for the water followed by one containing Dehydrite for the ammonia. Also, since $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ is quantitatively converted into $\text{Mg}_2\text{P}_2\text{O}_7$

on ignition, the residue could be weighed as a check upon the completeness of the decomposition.

APPARATUS.

The apparatus used for obtaining ammonia, from NH_4Cl and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ consisted of a purifying train, a silica tube in which the salts were heated, U-tubes containing the absorbent and a guard train which was connected to a water pump in order to draw a current of air through the apparatus. The purifying train contained a wash bottle of 18 M H_2SO_4 , a U-tube filled with Dehydrite and a similar tube filled with solid KOH. The guard train contained the same reagents. The tubes filled with Dehydrite and which were weighed had a diameter of approximately 1.2 cm. and when filled gave a column of absorbent about 15 cm. long.

The burettes and pipettes had been calibrated at the Bureau of Standards and the set of weights was calibrated by the author.

GENERAL PROCEDURES.

A. A sample of NH_4Cl was weighed into a porcelain boat, covered with soda-lime (labeled 20 mesh containing 2% H_2O) and quickly inserted into the silica tube. A current of air was drawn through the train and the silica tube heated gently with a Bunsen burner bearing a wing tip. Heat was applied for about 30 minutes after which the tube containing the ammonia was removed and the increase in weight determined or the ammonia was titrated. Soda-lime was used to assist in the evolution of ammonia and to react with the HCl formed and retain it in the boat. Blank runs made on the soda-lime showed (1) the absence of leaks in the train, (2) that the KOH effectively absorbed the water given off by the soda-lime and (3) that no ammonia was present in the reagents or apparatus. In weighing the U-tubes a similar tube was used as a tare.

B. A sample of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ was weighed into a porcelain boat and placed in the silica tube. The tube was heated gently for about ten minutes and then the heat gradually

increased to the highest obtainable with the Bunsen burner and maintained 20–30 minutes longer while air was drawn through the train as in A. With the size sample used 150–200 mg. of water were evolved which necessitated heating the side arm of the absorption tube nearest the silica tube from time to time to prevent condensation. This was done with a very small flame using a wash bottle tip connected to the gas supply with rubber tubing. The remainder of the procedure was the same as in A except that in runs in which both water and ammonia were determined the KOH tube was weighed before and after heating the $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ and at the end of the run the boat now containing $\text{Mg}_2\text{P}_2\text{O}_7$ was cooled in a desiccator and weighed to give a check upon the completeness of the ignition.

SPECIAL PROCEDURES.

Under this head are detailed the modifications of the general procedures which were used. The numbers in the first column of Tables IX and X refer to the procedures given here.

Procedure 1. Determination of NH_3 in NH_4Cl and in $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ by distillation and titration.

Weighed samples of the salt were transferred first to a beaker and dissolved in water, the $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ with the aid of 10 cc of N HCl, and the solution then transferred to a distillation flask. The contents of the flask were diluted to about 200 cc with recently boiled distilled water. A cork bearing a dropping funnel and Hopkin's distilling head was inserted and the latter connected with a condenser. The distillate was collected in 50.00 cc of standard 0.1 N HCl contained in a Volhard flask. 20 cc of 6 N NaOH were added through the dropping funnel. 125–150 cc of distillate were collected and the excess acid titrated with standard 0.1 N NaOH using methyl red as the indicator. The 6 N NaOH was boiled before use and only recently boiled distilled water was used. Connecting corks were covered with tin foil and blank determinations were made on the reagents.

Procedure 2. Weighing of NH_3 from NH_4Cl after absorption in Dehydrite.

A U-tube filled with Dehydrite and which had been brought to constant weight in the train was inserted after the KOH-tube following the silica tube. Samples of NH_4Cl (.1500-.2300 gm.) were weighed into porcelain boats. The sample was well spread out on the bottom of the boat which was quickly filled with soda-lime and immediately introduced into the center of the silica tube. The tube was heated gently and a current of air drawn through the train for about 30 minutes. Most of the ammonia was evolved within the first ten minutes as was evidenced by the heat given off during absorption. When the heating was finished the tube was removed, wiped off and allowed to stand near the balance 20-30 minutes before weighing.

Procedure 3. Titration of NH_3 from NH_4Cl after absorption in Dehydrite.

When this method was to be used only one limb of the U-tube was filled with a known amount of Dehydrite: this took 3-4 gms. of Dehydrite and gave a column 7-8 cm. long. After heating as in Procedure 2 the U-tube was removed from the train, the stopper of the empty limb removed and the grease wiped out of the neck. The contents were then emptied into a beaker containing an excess of standard HCl measured from a burette. 5-10 cc of the standard acid were then added to the tube which was tilted so that the acid came into contact with the entire surface of the closed limb and dissolved any particles of Dehydrite adhering to it. This acid was carefully poured into the beaker and the tube rinsed out several times with distilled water. The excess acid was titrated with standard 0.1 N NaOH. Correction was made for the acid used up by the Dehydrite.

Procedure 4. Absorption of H_2O and NH_3 from $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ in Dehydrite and titration of NH_3 .

Samples weighing from .3500-.5500 gm. were used. In this procedure the tubes containing KOH were omitted from the train and the weighed Dehydrite tube connected directly to the combustion tube. 4-5 gms. of Dehydrite were used. After the NH_3 and H_2O had been absorbed and the tube weighed the ammonia was titrated as in Procedure 3. With the quantity

of water absorbed (150–250 mg.) the Dehydrite caked somewhat at the surface nearest the combustion tube but no difficulty was experienced in transferring it to the acid for titration. Usually gentle tapping of the tube dislodged the caked material. If not, sufficient acid together with a drop of methyl red was added to seal the lower end of the U-tube and the tube inclined to bring the acid in contact with the Dehydrite. If the indicator changed color more acid was immediately added until an excess was present. When all had dissolved the contents were transferred to the beaker containing the remainder of the acid and the titration completed in the usual way.

Procedure 5. Distillation and titration of NH_3 from $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ after absorption in Dehydrite.

In order to make certain that the titration outlined in Procedure 4 gave all the ammonia that had been absorbed by the Dehydrite two samples, after they had been titrated, were distilled with NaOH . The NH_3 was absorbed in 0.1 N HCl and titrated as outlined in Procedure 1. The results checked the direct titration satisfactorily.

Procedure 6. Absorption of H_2O and NH_3 from $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ in pure $\text{Mg}(\text{ClO}_4)_2 \cdot \text{XH}_2\text{O}$ and titration of the NH_3 .

This procedure was the same as Procedure 4 except that pure magnesium perchlorate containing approximately 2–3 molecules of water was used in place of the commercial Dehydrite. The material was made by the partial dehydration of pure $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. It showed no alkalinity consequently there was no correction for this reagent.

Procedure 7. Absorption of H_2O in KOH and NH_3 in Dehydrite and the determination of both by weighing.

In this case the U-tube following the combustion tube as well as the Dehydrite tube was weighed before and after decomposition of the $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$.

Table IX shows the % NH_3 in purified NH_4Cl as determined by Procedures 1–3.

TABLE IX.

Theoretical: calculated from formula, NH_4Cl 31.83% NH_3 .

Procedure	Experiment No.	% NH_3
1.	A	31.84
1.	B	31.83
1.	C	31.77
1.	D	31.68
1.	E	31.79
1.	F	31.74
1.	G	31.88
Mean		= 31.79
Average deviation		= 2.1 pts./1000
Constant error (based on theoretical)		= 1.3 " " low.

Procedure	Experiment No.	% NH_3
2.	C	31.64
2.	E	31.71
2.	A ₂	31.86
2.	B ₂	31.77
2.	C ₂	31.74
2.	D ₂	31.83
2.	E ₂	31.90
Mean		= 31.78
Average deviation		= 2.2 pts./1000
Constant error (based on theoretical)		= 1.6 " " low.

3.	C	31.80
3.	E	31.77
3.	H	31.76
3.	J	31.71
3.	K	31.78
3.	L	31.73
3.	M	31.81
Mean		= 31.76
Average deviation		= .9 pts./1000
Constant error (based on theoretical)		= 2.2 " " low.

Constant error in the last two procedures using the mean result of Procedure 1 as the true value.

Procedure 2. Constant error	= .3 pts./1000 low.
Procedure 3. Constant error	= .9 " " low.

Table X gives the % NH_3 and % H_2O in $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ as determined by Procedures 1 and 4-7.

TABLE X.

Procedure	Experiment No.	% NH_3	
1.	1	6.69	
1.	2	6.71	
1.	3	6.65	
1.	4	6.68	
Mean		= 6.68	
Average deviation		= 2.6 pts./1000	
4.	3	6.57	
4.	A	6.62	
4.	C	6.51	
4.	D	6.55	
4.	E	6.54	
4.	F	6.55	
4.	H	6.52	
4.	J	6.50	
4.	K	6.62	
4.	L	6.55	
4.	N	6.56	
4.	O	6.53	
4.	A ₂	6.53	
4.	B ₂	6.58	
4.	C ₂	6.53	
Mean		= 6.55	
Average deviation		= 4.0 pts./1000	
5.	N	6.55	
5.	O	6.53	
Mean		= 6.54	
6.	H	6.52	
6.	J	6.50	
6.	K	6.62	
6.	L	6.55	
Mean		= 6.55	
Average deviation		= 4.0 pts./1000	
7.	A	6.73	% H_2O 48.51
7.	B	6.75	48.22
7.	C	6.66	47.98
7.	D	6.77	48.14
Mean		= 6.73	= 48.2
Average deviation		= 4.8 pts./1000 = 3.1	

The percentage of H_2O in $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ obtained by subtracting the percentage of NH_3 (distillation method) from the loss in weight on ignition of the salt is 47.99%.

TABLE XI.

In this table are shown the results for the determination of ammonia and water together by (1) absorption in Dehydrite and (2) loss in weight of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ on ignition.

	$\text{H}_2\text{O} + \text{NH}_3$ %
1. Mean of 13 determinations with average deviation of 3 pts./1000	= 54.68
2. Mean of 16 determinations with average deviation of 0.7 pts./1000	= 54.67
Loss in weight on ignition 14 experiments	= 3.5806 gms.
Gain in weight in U-tubes 14 experiments	= 3.5768 gms.
Difference	= 0.0038 gm.

DISCUSSION OF RESULTS.

The results obtained with NH_4Cl are to be regarded as more reliable than those obtained with $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ for the following reasons:

1. NH_4Cl can be obtained in a pure condition more readily than $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. It can be purified by sublimation and recrystallization whereas the phosphate cannot.

2. The composition of NH_4Cl is not dependent upon a carefully controlled set of conditions as in the case of the phosphate. The latter salt, for example, must be dissolved with the aid of acid and reprecipitated with proper regard to the concentration of hydrogen ion and ammonium salts and to temperature.

3. Ammonium chloride can be dried above 100°C while the hexahydrate loses water above 30°C or in a desiccator over calcium chloride.

4. Using the method of distillation with NaOH (Procedure 1, Tables IX and X) followed by titration as a standard the analytical results show that the NH_3 content of the NH_4Cl employed to be nearer the theoretical value than in the phosphate.

When the analytical results obtained by the new method using Procedures 2 and 3 are compared with the standard method the agreement is seen to be entirely satisfactory and there is little choice between weighing the NH_3 (Procedure 2) and titrating it (Procedure 3). The results of Procedure 2 show a smaller constant error but a larger average deviation.

Determinations $\text{A}_2\text{-E}_2$ and J-M were made rapidly, without any special precautions, in order to test the method as a routine procedure. Each determination was completed within an hour.

Although the two procedures (2 and 3) give the same analytical results each has certain advantages over the other. When the NH_3 is weighed (Procedure 2) more elaborate precautions must be taken with regard to the purifying train. Moisture must, of course, be kept out of the tube in which the NH_3 is collected. The Dehydrite tube must be brought to constant weight in the train, must be handled carefully and weighed accurately both before and after the determination. These operations take time and care. On the other hand, the tube can be filled with Dehydrite and used for many determinations before refilling. This is an advantage and requires less Dehydrite per determination. Furthermore the Dehydrite can be recovered, if desired, by applying heat and vacuum.

When the ammonia is titrated the only precaution necessary so far as the train is concerned is that extraneous NH_3 be kept out which is readily accomplished by merely having a tube of Dehydrite in the purifying train. The presence of moisture has no effect upon the results provided, of course, that the amount does not exceed the capacity of the Dehydrite to absorb both water and ammonia. In order to economize on Dehydrite, however, and to facilitate its transfer to the acid prior to titration it has been found desirable to remove the water if it is present in large amount by passing the gases through KOH. As noted above the presence of considerable water causes the Dehydrite to cake in the absorption tube. The titration can be made immediately after the heating is completed. The tubes must be dried and charged with known amounts of Dehydrite before each determination. If several tubes are kept in use this is not a serious objection: the fill-

ing is easily done and the weight need be obtained only to the nearest centigram. A considerable excess of Dehydrite must be used and this reagent is rather expensive. The transfer of the Dehydrite to the acid requires some care but it is not at all difficult after a little practice. The usual form of U-tube with ground glass stoppers has been found to work admirably.

COMPARISON OF THE NEW METHOD WITH THE STANDARD METHOD.

When the new method is compared with the standard method of distillation and absorption in standard acid it is seen to have certain advantages. The absorbent for the new method is a solid and the ammonia can be weighed directly if desired. The absorbent for the standard method is a solution and must be standardized. The new method admits of a choice of two procedures; one gravimetric and the other volumetric while for the standard method there is but one, volumetric. In the standard method a blank distillation must be made to correct for the reagents which takes longer than to determine the alkalinity of the Dehydrite. The new method offers the possibility of determining water and ammonia simultaneously whereas the standard method does not. With regard to the time consumed and the apparatus and technique required there is little choice between the two. The new method offers a rapid, precise procedure which can be used as a check upon the standard method.

RESULTS OBTAINED WITH $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$.

The results obtained with $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ and the partially dehydrated salt, shown in Tables X and XII, are to be regarded as showing the possibility of applying the method to the determination of ammonia in the presence of water and to the simultaneous determination of both rather than as additional data for the establishment of the new method. The uncertainty of the composition of the hexahydrate and the partially dehydrated salt and the fact that the latter is somewhat hygroscopic preclude their use in this way.

When account is taken of the fact that in the determinations made upon the hexahydrate from 150–250 mg. of water and only 25–35 mg. of ammonia were evolved and absorbed the average deviations are quite satisfactory. The same cannot be said of the constant error taking the distillation method (Table X, Procedure 1) again as the standard. The constant error so obtained is 19 pts./1000 low. For the size samples used, however, this amounts to a loss of only about 0.5 mg. of NH_3 per determination.

An explanation for this large constant error and the fact that it is low has not been found. The 4 determinations of NH_3 by distillation and titration represent the use of two different sets of reagents and standard solutions. The average deviation is satisfactory and furthermore this method gave no difficulty with the other materials. Therefore the mean value of 6.68% NH_3 can be considered reliable and representing the ammonia content of this substance. When two tubes containing Dehydrite were used in tandem, no gain in weight of the second was observed hence, no loss of ammonia occurred in that way. The loss in weight of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ on ignition and the gain in weight of the U-tubes (Table XI) indicate that all the ammonia and water were absorbed in the Dehydrite. The fact that determinations N and O (Procedures 4 and 5) gave the same value for ammonia on titration before and after distillation shows that all the ammonia absorbed by the Dehydrite is titratable. In determinations $\text{A}_2\text{--C}_2$ (Procedure 4) water was absorbed in KOH and only ammonia entered the Dehydrite tube. Again the same results were obtained. The results of Procedure 7 where both water and ammonia were determined simultaneously are high. Electrolytic KOH which had been crushed and sifted to get rid of fine dust was used. The pieces were uneven in size and there were many voids in the tube and it is possible that some water got by and was weighed as ammonia. More work is necessary before the method can be regarded as satisfactory for this determination. Fused, granular KOH or KOH mounted on asbestos fibers similar to "Ascarite" (a NaOH-asbestos mixture)

might work better. It might well be also that another form of absorption tube would be better in this case.

For the purpose of trying out the method on a material which would yield water and ammonia in more nearly equal proportions a quantity of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ was heated in an oven to $50\text{--}55^\circ\text{C}$ for a week. During the heating the salt lost some ammonia as well as water. The ammonia was determined by some of the same procedures used with the other materials.

The procedures and results are shown in Table XII.

TABLE XII.

Procedure	Number of determinations	Mean % NH_3	a.d. pts./1000
1.	2	5.39	0
2.	4	5.30	6.6
3.	4	5.28	5.7

Procedures.

1. Distillation of sample with NaOH followed by titration.
2. Absorption in Dehydrite followed by titration.
3. Absorption in Dehydrite followed by distillation with NaOH and then titration.

Using the value (5.39% NH_3) obtained by Procedure 1 as a standard, the values obtained by absorption in Dehydrite and titration (Procedures 2 and 3) are low with about the same constant error as was obtained with the hexahydrate.

The average deviation in the results of Procedures 2 and 3 are somewhat greater than those obtained with the hexahydrate. The fact that the partially dehydrated hexahydrate is hygroscopic probably accounts for this.

The results obtained by Procedures 2 and 3 agree with each other satisfactorily thus giving additional evidence that all of the ammonia absorbed by the Dehydrite is titrated by the procedures outlined above.

SUMMARY.

1. Magnesium perchlorate has been shown to form a stable hexammine and diammine.

2. The densities of the hexammine and diammine have been determined and their molecular volumes calculated.

3. The vapor pressure curve and the isothermal decomposition curve for the hexammine have been determined.

4. A new method for the determination of ammonia has been developed and the possibility of employing $\text{Mg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ to the simultaneous determination of both water and ammonia has been indicated.

This investigation is a portion of a larger problem in which it is proposed to investigate the preparation and properties of the perchlorate amines of calcium, strontium and barium and also the amines of the other oxygen-halogen acids of these elements and of magnesium. Preliminary work has shown that all of the anhydrous perchlorates combine with ammonia and that amines are formed with barium, calcium and magnesium chlorates. The reaction of ammonia with strontium chlorate has not yet been tried.

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